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REPORT No. 8/R/69

A New Process
for the Manufacture of Styphnic Acid

[R]

D.A. Salter
R.J.J. Simkins

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A New Process
for the Manufacture of Styphnic Acid

by

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D.A. Salter and R.J.J. Simkins

SUBJECT	PROJECT NUMBER
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3	III
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3.2	V Project No.
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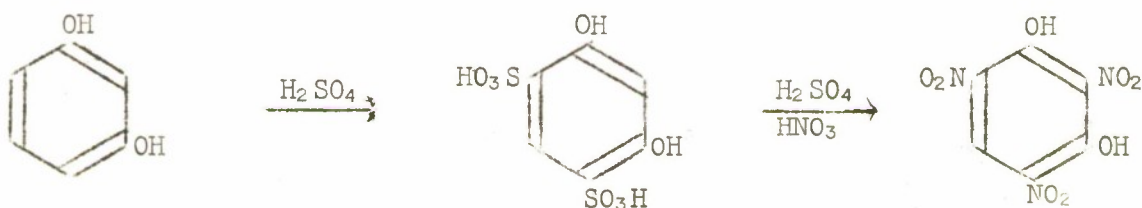
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1. SUMMARY

A new process has been developed for the manufacture of styphnic acid (2,4,6-trinitroresorcinol). Resorcinol is treated with dilute nitric acid and sodium nitrite to give 2,4-dinitrosoresorcinol, and the latter is pumped as a slurry into hot concentrated nitric acid, in which it undergoes oxidation and nitration to yield styphnic acid (90 per cent). The process has been evaluated in collaboration with ROF, Bridgwater, and appears to be more convenient and economical than the conventional sulphonation/nitration method.

2. INTRODUCTION

Styphnic acid is usually manufactured by a two-stage process involving sulphonation of resorcinol and subsequent nitration with mixed acid (1 - 6).

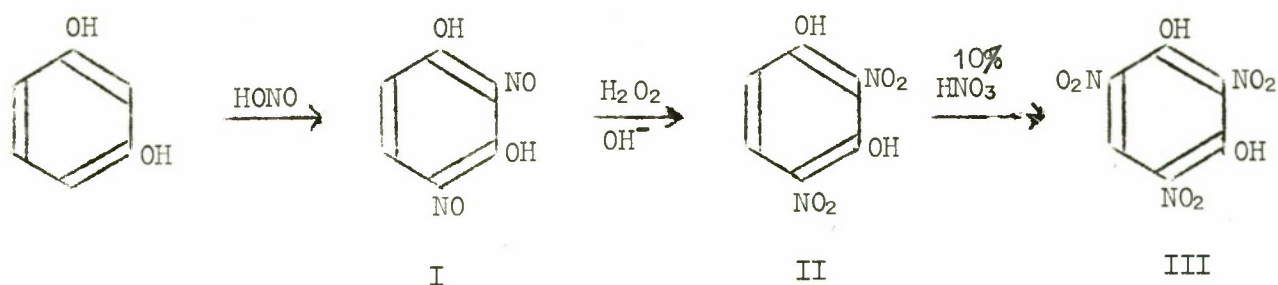


Whilst the process is straightforward when carried out on a small scale (7), difficulties associated with stirring the pasty sulphonation mixture, and with a tendency to foaming in the subsequent nitration, make large-scale manufacture troublesome. Aubertin and Emeury (6) investigated this aspect, and concluded that foaming is associated with oxidation of unsulphonated resorcinol, and that there is a greater tendency towards foaming when the crystal size of the styphnic acid is small. Since styphnic acid is almost insoluble in the nitration medium, it was concluded that growth of relatively large styphnic acid crystals (and hence reduced foaming) could only be achieved by slow nitration.

In an investigation in this laboratory (8) into the manufacture of 2,4-dinitroresorcinol (DNR), we found that DNR rejected because of bad colour could be converted into high quality styphnic acid simply by boiling with dilute nitric acid.

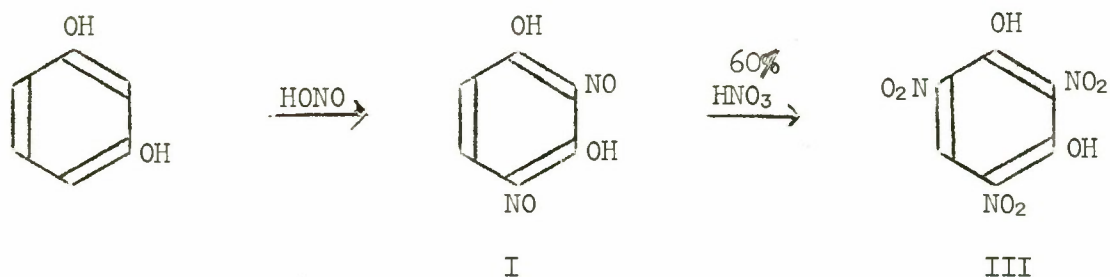
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This reaction is not novel (9), but it did offer the possibility of eliminating sulphonation of resorcinol as a necessary step in the manufacture of styphnic acid.

While 2,4-dinitroresorcinol (II) is best made by the alkaline oxidation of a freshly prepared slurry of 2,4-dinitrosoresorcinol (I), ice-cold 50 per cent nitric acid may also be used for the oxidation (10). Jones and Roberts (11) have defined the conditions under which dinitrosoresorcinol (I) may be oxidized and nitrated to styphnic acid (III) by the action of hot nitric acid. A similar process has been used by Indian workers (12). Both these processes involve the preparation of dinitrosoresorcinol (I) by nitrosation of resorcinol in dilute sulphuric acid; the intermediate I is isolated and washed with water before further reaction in hot concentrated nitric acid.



We found that isolation of dinitrosoresorcinol involves lengthy filtration, during which the intermediate decomposes slightly, with a resultant adverse effect on the yield and quality of the styphnic acid.

We have modified the process by using dilute nitric acid as the medium for the nitrosation stage, thus removing any possibility of sulphates contaminating the final styphnic acid. We have also eliminated the filtration step by pumping the slurry of dinitrosoresorcinol into hot concentrated nitric acid, where it undergoes immediate oxidation with no induction period.

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On a laboratory scale the time required to achieve a 90 per cent yield of styphnic acid is only 4 hours, compared with over 10 hours required for a similar yield by sulphonation/nitration. On a plant scale 60 kg of styphnic acid have been produced per 5 hours. As well as offering the prospect of increased rate of production, the process requires relatively simple plant, no mixed acid facilities, and presents no corrosion problems with stainless steel.

A further advantage of the nitrosation/oxidation process is that the product is sulphate-free and sufficiently pure to be used for lead salt (initiator) manufacture without further purification.

3. METHODS

Initial experiments were made on a molar scale using the sulphonation/nitration method (3,5). Considerable difficulties were encountered with stirring, and with foaming, and in some cases it was not possible to add the last 25 per cent of the nitrating acid without excessive local overheating (in one experiment the temperature rose suddenly from 50 to over 100°C). Experiments were made to establish whether initial sulphonation was necessary, and it was found that a good yield of styphnic acid could be obtained by merely dissolving resorcinol in concentrated sulphuric acid, followed by immediate nitration at 50°C. Highly coloured intermediates were produced by this method, and the colour of the styphnic acid obtained was variable.

Most subsequent experiments involved treating a dilute nitric acid solution of resorcinol with sodium nitrite to give 2,4-dinitrosoresorcinol (DnR), followed by treatment with hot concentrated nitric acid to convert DnR into styphnic acid. It was found that addition of the nitric acid to the DnR slurry resulted in uncontrolled oxidation, accompanied by a vigorous fume-off. Much better control was obtained by adding the DnR slurry to hot nitric acid.

Experiments in which DnR was isolated showed that filtration was tedious, even when the process was simplified by use of an immersion filter to remove only half of the liquor. Reduction of the volume of liquor used in nitrosation eliminated the concentration step, permitting the DnR slurry to be added directly to the oxidizing acid.

The crude styphnic acid was initially purified by digestion with fuming nitric acid (12). This method gave a very pure product, pale cream in colour, with a very high melting point (180°C). The very high solubility of styphnic acid in fuming nitric acid led to poor recovery unless nitric acid saturated with styphnic was used (and the liquor kept for subsequent digestions), or alternately the liquor was drowned on ice/water to precipitate a second crop. Experience in this work has shown that a solution of styphnic acid in fuming nitric acid is not stable: at best the styphnic acid is fairly rapidly decomposed, and under some conditions it may be dangerous, for the solution

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can adiabatically self-heat to the point of fume-off. An investigation into the use of fuming nitric acid for purifying polynitrophenols has been reported separately (13).

4. EXPERIMENTAL

Melting points were determined on a Kofler hot-stage microscope, and in a Mettler automatic apparatus. Liquid and slurry transfers were made by a peristaltic pump.

4.1 Preparation of Styphnic Acid (Table 3, Expt. No. 17)

In a 3 l flask, fitted with anchor stirrer, thermometer, and external water bath, 110 g resorcinol (1.0 mole) was dissolved at room temperature in a solution of 68 ml fuming nitric acid (d 1.5, 1.61 mole) in water (325 ml). Crushed ice (1500 g) was added, and a solution of 150 g sodium nitrite (2.18 mole) in water (370 ml) pumped in, at a rate such that the temperature of the vigorously stirred mixture remained below 5°C (ca. 20 min); ice/water in the external bath helped control the temperature, but was not essential.

The resultant slurry was aged at 5°C for 30 min, then pumped into a similar reaction vessel containing 400 ml hot nitric acid (d 1.37, 5.2 mole). The temperature of the oxidizing mixture was kept at 55 - 60°C by sparging steam into the water bath, and by adjusting the rate of addition of the cold dinitrosoresorcinol slurry. The copious nitrous fumes evolved in the early stages were removed by drawing a stream of air through the flask. Addition complete (30 min), the mixture was aged at 60°C for 30 min, then heated to 95°C over 45 min, cooled to room temperature, and pumped into a sintered polythene filter to separate styphnic acid. The product was washed with water (4 × 250 ml) and air-dried at 40°C; yield 90.5 per cent.

4.2 Recrystallization of Styphnic Acid

Dry crude styphnic acid (225 g) was added to 500 ml fuming nitric acid (d 1.5, saturated with styphnic acid) and stirred vigorously for 30 min, using an external water bath to maintain a temperature of ca. 20°C. The mixture was filtered, the liquor being kept for the next experiment, and the styphnic acid was washed with water (6 × 250 ml) and air-dried. Although material purified in this manner has a very light colour, high melting point, and good IR spectrum, on storage it develops a noticeable nitric acid odour. This is more pronounced when the crystal size is large and is probably due to occluded nitric acid. Such acidic material was suspended in water (2 ml/g) and stirred vigorously while being heated on a steam bath for 1.5 hours, before being cooled, filtered, and washed with water (4 × 250 ml); recovery 97 per cent.

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4.3 Melting Point of Styphnic Acid

When the melting point is determined on a hot-stage microscope it is often found that individual crystals of crude styphnic acid show a double melting point, melting first at ca. 168°C, then recrystallizing and melting again at 179°C. Alternately some crystals melt at 168°C, while others sublime onto the cover slip and there melt at 179°C. In a capillary tube (Mettler apparatus) it was generally the upper melting point that was recorded, although occasionally one of a triplicate sample would melt at ca. 170°C. It seems likely that the initial product contains the unstable trigonal polymorph (14), which transforms to the stable monoclinic form. Nitric acid digestion gives the stable form.

4.4 Large Scale Production

Over 400 kg of styphnic acid have been manufactured at ROF Bridgwater using this process. Details of a typical run are as follows.

A large stainless steel reaction vessel, fitted with propeller stirrer, was charged with 45 l water, 60 kg of ice cubes, and 19.2 l nitric acid (d 1.40, 294 mole). After dissolving 14.7 kg resorcinol (134 mole) in this mixture, a solution of 20 kg sodium nitrite (288 mole) in 45 l water was added from a head tank, while more ice (95 kg in all) was added in 12 kg lots to maintain the temperature below 5°C. Ten minutes after the addition was complete the slurry of dinitrosoresorcinol was pumped into a similar reaction vessel containing 51.2 l hot nitric acid (d 1.40, 737 mole). The temperature was maintained at $62^{\circ} \pm 3^{\circ}\text{C}$ throughout the addition by use of cooling water in the coils of the reaction vessel and steam in its jacket. Addition complete, the mixture was heated at 98°C for 1.3 hours, then cooled, and the styphnic acid filtered, washed with water (2 x 50 l), and air-dried; yield 31.6 kg (96 per cent).

The batch size in similar production development runs has ranged from 18 to 61 kg of styphnic acid; the strength of the oxidizing nitric acid has been varied from 50 to 65 per cent.

5. DISCUSSION

The experimental conditions used for the preparation of styphnic acid, are summarized in Tables 1 - 4, and typical analytical data are given in Table 5.

5.1 Nitrosation

In early experiments (1 - 10) nitrosation was carried out in quite dilute solution, and it was thought necessary to remove some of the liquor before oxidizing the dinitrosoresorcinol. The varying yields obtained in the first four experiments indicate that isolation of DnR is undesirable.

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The ease with which DnR slurries could be filtered varied markedly (cf. expts 6 - 10), even when the process conditions were supposedly identical. Reduction of the volume of liquids used for nitrosation eliminated the need for filtration, and improved the yield (cf. expts 10, 11, 17, 18).

Most of this work was done using insufficient nitric acid to generate 2 moles of nitrous acid (from the excess sodium nitrite) per mole of resorcinol. This course was chosen to ensure that there would be freshly generated nitrous fumes when the dinitrosoresorcinol slurry was added to the oxidizing medium, thus obviating any induction period. The styphnic acid produced in the laboratory seemed satisfactory, but development work at ROF, Bridgwater suggested that a lighter-coloured styphnic acid is obtained when 2 moles of nitrous acid are generated in the nitrosation stage. The proportions were accordingly changed for later work.

Although nitrosation of resorcinol has hitherto been performed in dilute sulphuric acid (7,9,11), the work reported here shows that dilute nitric acid may be substituted, with resulting advantages in yield, ease of handling, reduction of plant corrosion, and purity of ultimate product. The yield of dinitrosoresorcinol was found to be stoichiometric.

5.2 Oxidation/Nitration

The oxidation temperature is easily controlled by means of simple external cooling, and by varying the rate of addition of the cold dinitrosoresorcinol slurry. The heat evolved during the initial oxidation increases with the strength of nitric acid used, but over the range 50 - 70 per cent nitric acid there was no evidence that the reaction could become uncontrollable. When initial oxidation is complete, the subsequent nitration is endothermic.

The apparent yields obtained when digestion liquor was used to make up the oxidizing medium (expts 12 - 16) are very high, and should be reduced by a factor to allow for the extra styphnic acid introduced by the liquor. Since it has been found that a solution of styphnic acid in fuming nitric acid is not stable, and since the history of the digestion liquors used was not recorded, it is impossible to quantify the correction factor; a value of 5 per cent might be appropriate.

Examination of the results in Table 4 suggests that an optimum yield of styphnic acid is obtained when 60 per cent nitric acid is used as the oxidizing medium, with a mole ratio of nitric acid/dinitrosoresorcinol of at least 5.0. Other work (8) has shown that under the right conditions the yield of dinitrosoresorcinol is practically 100 per cent.

In an experiment in which a freshly prepared solution of styphnic acid in nitric acid (d 1.5) was used to prepare 60 per cent oxidizing acid, and then 6 per cent aqueous sodium nitrite solution added at 60°C in simulation of the oxidation process, the styphnic acid was recovered quantitatively. This demonstrates that styphnic acid is not destroyed in the oxidation stage.

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5.3 Purity of Product

Styphnic acid produced in laboratory experiments was analyzed by Chemical Inspectorate, Bishopton, according to specification CS 1936B. The results obtained (cf. Table 5) suggest that the crude product is reasonably pure, and that material recrystallized from fuming nitric acid has a very high purity. Subsequent work has shown that the crude material is sufficiently pure to be used directly in the preparation of lead salts (initiators). The main effect of the nitric acid digestion is to improve the colour value, and to lower the percentage of toluene-insoluble material. There is no discernable difference in the styphnic acid obtained from Analar resorcinol and that from various technical grades.

6. ACKNOWLEDGMENTS

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TABLE 1

Small Scale Preparation of Styphnic Acid

30 g A.R. Resorcinol (0.273 mole) nitrated with 100 ml 40% Sodium Nitrite (0.57 mole)

Expt. No.	Nitrosation Stage					Oxidation Stage		Crude Product		Pure Styphnic		Remarks
	Nitric Acid		Water, ml	Ice, g	Mole Ratio HNO ₃ /NaNO ₂ /Resorcinol	Nitric Acid ml	Mole Ratio HNO ₃ /DnR	Yield, %	M.p., °C	Recovery, %	M.p., °C	
	ml	%				%						
1	18	99	450	600	1.6/2.1/1.0	100	4.56	53	177	87	179	DnR was isolated and stored overnight as aqueous slurry before oxidation - some decomposition apparent. Digestion liquor drowned for 2nd crop.
2	18	98 H ₂ SO ₄	450	600	1.6/2.1/1.0	100	4.56	86	178	89	179	H ₂ SO ₄ used for nitrosation. Intermediate isolated, washed, used as quickly as possible.
3	18	99	450	600	1.6/2.1/1.0	100	4.56	72	167/177	28	178	Delay in isolating intermediate. Liquor from digestion used for No. 4 digestion.
4	18	99	450	600	1.6/2.1/1.0	110	5.0	82	165/175	105	179	Filtered 50% nitrosation liquor with immersion filter, then added slurry to oxidation nitric.
5	18	99	450	600	1.6/2.1/1.0	110	5.0	84	168/178	-	-	Filtered 60% of nitrosation liquor, then added slurry to oxidation nitric. No purification tried.

TABLE 2

Preparation of Pure Styphnic Acid

110 g A.R. Resorcinol (1.0 mole) nitrated with 370 ml 40% Sodium Nitrite (2.18 mole)

Expt. No.	Nitrosation Stage				Oxidation Stage			Crude Product	Pure Styphnic		Remarks	
	Nitric Acid	Water, ml	Ice, g	Mole Ratio HNO ₃ /NaNO ₂ /Resorcinol	Mole Ratio HNO ₃ /DnR	Yield, %	Recovery, %		M.p., °C			
										ml		%
6	68	99	1650	2000	1.61/2.18/1.0	370	60	4.9	82	134	179	2.5 l nitrosation liquor filtered prior to oxidation. Crude product digested with 500 ml HNO ₃ (d 1.5) satd. with styphnic.
7	68	99	1650	2000	1.61/2.18/1.0	370	60	4.9	85	106	179	2.3 l nitrosation liquor filtered, but filter clogging led to delay. Crude product digested with liquor from 6 (ad 500 ml).
8	68	99	1650	2000	1.61/2.18/1.0	370	60	4.9	83	110	180	2.2 l nitrosation liquor filtered with some delay. Crude product digested with liquor from 7 (ad 500 ml).
9	68	99	1650	2000	1.61/2.18/1.0	370	60	4.9	85	100	180	2.8 l nitrosation liquor filtered very easily. Crude product digested with liquor from 8 (ad 500 ml).
10	68	99	1650	2000	1.61/2.18/1.0	370	60	4.9	77	98	180	1.5 l nitrosation liquor filtered with much delay. Crude product digested with liquor from 9 (ad 500 ml).
11	68	99	825	1000	1.61/2.18/1.0	370	60	4.9	88	98	179	Because of reduced initial volume no filtration needed. Crude product digested with liquor from 10 (ad 500 ml).

/TABLE 3

TABLE 3

Preparation of Crude Styphnic Acid

110 g Technical Resorcinol (1.0 mole) nitrosated with 370 ml 40% Sodium Nitrite (2.18 mole)

Expt. No.	Nitrosation Stage					Oxidation Stage		Crude Product		Remarks
	Nitric Acid		Water, ml	Ice, g	Mole Ratio HNO ₃ /NaNO ₂ /Resorcinol	Digestion Liquor ^a , ml	Water, ml	Yield, %	M.p., °C	
	ml	%								
12	68	99	825	1000	1.61/2.18/1.0	250	150	99.5	168/179	GPR Resorcinol used. Oxidation medium made from stock of nitric acid (d 1.5) saturated with styphnic + liquor from 11.
13	68	99	825	1000	1.61/2.18/1.0	250	150	96.0	169/179	Identical with 12.
14	68	99	325	1500	1.61/2.18/1.0	250	150	95.5	169/180	Ratio of ice/water in nitrosation changed, but otherwise identical with 12.
15	68	99	325	1500	1.61/2.18/1.0	250	150	97.0	169/179	Resorcinol and NaNO ₂ from ROF, Bridgwater; otherwise identical with 14.
16	68	99	325	1500	1.61/2.18/1.0	250	150	97.5	167/179	Identical with 15.
17	68	99	325	1500	1.61/2.18/1.0	400 (60% HNO ₃)		90.5	167/179	Oxidation medium made with fresh 60% HNO ₃ ; otherwise identical with 14.
18	100	70	300	1500	1.61/2.18/1.0	400 (60% HNO ₃)		90.0	166/177	Technical Resorcinol used; nitrosation medium made with 70% HNO ₃ ; otherwise identical with 17.

^aMole ratio HNO₃/DnR was 5.2 in expts 17,18; probably about 5.0 when using digestion liquor

TABLE 4

Large Scale Production of Crude Styphnic Acid

Expt. No.	Nitrosation Stage				Oxidation Stage		Crude Product		
	Nitric Acid		Water, ml	Ice, g	Mole Ratio HNO ₃ /NaNO ₂ /Resorcinol	Nitric Acid		Yield, %	M.p., °C
	ml	%				ml	%		
330 g Technical Resorcinol (3.0 mole) nitrosated with 1110 ml 40% Sodium Nitrite (6.5 mole)									
19	300	70	1000	4500	1.58/2.17/1.0	1000	70	5.26	169/179
20	300	70	1000	4500	1.58/2.17/1.0	1150	60	5.05	167/179
21	300	70	1000	4500	1.58/2.17/1.0	1150	60	5.05	166/180
110 g Resorcinol (1.0 mole) nitrosated with 370 ml 40% Sodium Nitrite (2.18 mole)									
22	85	99	325	1500	2.01/2.17/1.0	400	60	5.50	168/179
23	85	99	325	1500	2.01/2.17/1.0	400	50	4.16	167/176

TABLE 5
Analysis of Styphnic Acid Samples

Expt. No.	M.p., °C	Nitrate %		Chloride, %	Sulphate, %	Toluene Insoluble, %	Sulphated Ash, %	Colour Value
		DPA ¹	Xyle ²					
1	178.7	Nil	Nil	< 0.01	< 0.01	0.10	< 0.01	0.18
2	177.5	Nil	Trace ³	< 0.01	< 0.01	0.39	< 0.01	0.20
3	177.2	Nil	Nil	< 0.01	< 0.01	0.43		0.20
4	177.8	Nil	Nil	< 0.01	< 0.01	0.32		0.20
5	179.0	Nil	Nil	< 0.01	< 0.01	0.13		0.14
6	178.4	Nil	Trace	< 0.01	< 0.01	< 0.01		0.05
7	178.2	Nil	Nil	< 0.01	< 0.01	< 0.01		0.04
8	178.3	Nil	Nil	< 0.01	< 0.01	< 0.01	< 0.01	0.04
9	179.3	Nil	Nil	< 0.01	< 0.01	< 0.01		0.04
9u	178.9	Nil	Trace	< 0.01	< 0.01	< 0.01		0.04
10	179.2	Nil	Trace	< 0.01	< 0.01	0.04	Nil	0.04
10u	179.9	Nil	Nil	< 0.01	< 0.01	0.03	Nil	0.04
11c	177.4	Nil	Nil	< 0.01	< 0.01	0.39		0.20
11	179.5	Nil	Nil	< 0.01	< 0.01	0.05	Nil	0.05

Samples 1 - 5 and 11c were crude styphnic acid; the rest were purified by digestion with fuming nitric acid.

Samples 9u and 10u were digested with fuming nitric, but wash was omitted.

Footnotes: ¹Estimated by Diphenylamine/sulphuric acid.

²Estimated by nitration of 2,4-xylencol.

³Trace: colour less than that from 0.01% standard.

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